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(54) **Core-shell polymer**

Kern-Schale-Polymer

Polymère coeur-enveloppe

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EP-A- 0 115 373 **EP-A- 0 192 356**
EP-A- 0 234 063 **EP-A- 0 338 303**
US-A- 4 086 300

EP 0 494 534 B1

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Description

The present invention relates generally to the field of low gloss polyacetal resin compositions. More specifically, the present invention relates to the preparation of core-shell polymers which are especially useful as agents to reduce the surface gloss characteristics of molded resin articles (e.g. polyacetal resin), and to equally novel polyacetal molding compositions which include an effective amount of such core-shell polymers. Molded articles of the composition are also provided.

Polyacetal resin is used in diverse fields as an engineering plastic due to its excellent physical properties, such as mechanical, electrical and chemical properties (e.g. chemical- and heat-resistance). However, the identification of new end-use applications for polyacetal resins often requires further property alterations and/or enhancement.

One such property that is needed when polyacetal resin is employed to form molded parts used for automotive trim or optical instruments is a relatively low surface gloss. A low surface gloss will thus reduce the light reflectivity property of the molded part. As a result, low surface gloss on molded parts will tend to cause less eye irritation (i.e. since less light will be reflected from the part's surface). Furthermore, low surface gloss on molded parts fabricated from engineering plastics tends to give the part a more aesthetically pleasing high-grade appearance.

An ability to "engineer" the surface gloss characteristics would also be beneficial in those instances where molded parts fabricated from polyacetal resin (which inherently exhibits a relatively high surface gloss) are used in cooperation with molded parts formed of other, non-polyacetal, resins. It is especially desirable to reduce the surface gloss of polyacetal resin to an level substantially equivalent to that of molded parts of the non-polyacetal resin in which it is cooperatively used. Inability to reduce the surface gloss of polyacetal resins by controlled amounts so that it is visually imperceptible with parts molded from non-polyacetal resins has thus hitherto been a barrier to using polyacetal resin in end-use applications (e.g. as parts for electrical and electronic devices) where the polyacetal part will be visible.

Attempts in the past to reduce the inherently high surface gloss of polyacetal resins have included incorporating inorganic filler material, such as calcium carbonate or talc, in a polyacetal base resin. However, large amounts of such inorganic filler material must typically be added to the polyacetal base resin before the desired low surface gloss appearance is realized. The addition of relatively large amounts of inorganic filler material, however, is disadvantageous since it has a tendency to reduce the mechanical characteristics (especially elongation and toughness) normally associated with polyacetal resins. Thus, for example, the mechanical properties may be degraded by the addition of relatively large amounts of filler material to the point where molded parts of such a highly filler-loaded polyacetal resin breaks during assembly or when dropped.

It has also been proposed to lower the surface gloss characteristics of polyacetal articles by incorporating an organic filler material in the form of cross-linked acrylic resin particles. However, this technique is less than satisfactory in terms of the resulting gloss reduction that is achieved. Furthermore, the addition of acrylic resin increases the likelihood that the polyacetal resin may decompose when the acrylic resin particles are melt-blended. Such decomposition of a polyacetal occurs during blending, kneading or melt-blending.

Thus, what has been needed is a polyacetal resin composition having reduced surface gloss characteristics which can be engineered without affecting the desirable physical properties of polyacetal resins generally. It is towards fulfilling such a need that the present invention is directed.

We have found that this problem of reducing the surface gloss of a polyacetal resin composition without deleteriously affecting the desirable physical properties of the polyacetal resin may be alleviated by making use of specific core-shell polymers with the polyacetal resin. Certain core-shell polymers have previously been described US-A-4200567 and JP-A 2-294352. Other core shell polymers are known from, for example, EP-A-0 234 063 which proposes the addition to a polyamide/polyphenylene ether mixture, in order to promote impact resistance, of, *inter alia*, "core-shell polymers having a rubber-like core and one or more shells. For this purpose, reference may be made, for example, to US-A-3,808,180; 4,096,202; 4,180,494; 4,306,040, 4,375,532 and 4,495,324. Core-shell polymers generally comprise a rubber-like core, for example mainly constructed from a diene rubber, for example polybutadiene rubber, or mainly from an acrylate rubber, for example, poly n-butylacrylate. The rubber of the core may moreover comprise one or more comonomers. The core may be cross-linked by carrying out the preparation of the core in the presence of cross-linking agents. As cross-linking agents may be used bifunctional unsaturated compounds. One or more shells have been provided on the core, of which generally at least one is formed from a glassy, i.e. non-rubber-like polymer or copolymer. The shell or shells is or are generally built up from one or more of the following monomers: alkylmethacrylates, alkylacrylates, acrylonitrile, vinylaromatic compounds, for example styrene or substituted styrene compounds, for example alphasubstituted styrene or halogenated styrene compounds. The shell may be 'bonded' to the core via graft linking agents which may be present in the core and/or shell. The preparation of core shell polymers is generally known; for this purpose, reference may be made, for example, to the United States Patent Specifications mentioned hereinbefore."

As mentioned, however, the addition of the core-shell polymer is to a polyamide/polyphenylene ether mixture, and for the purpose improving impact resistance. It is also known, for example from EP-A-0 192 356, to add certain core-

shell polymers to polyacetal resin compositions for promoting impact resistance in an article to be metallized.

Broadly the present invention is directed to a method of producing a novel core-shell polymer which may be incorporated into a polyacetal resin composition as a surface gloss reduction (SGR) agent, and to polyacetal resin compositions which include an effective surface gloss reducing amount of the novel core-shell polymer. In this connection, the core-shell polymer which is employed as the SGR agent is one which has a rubbery polymer core and a glassy (amorphous) polymer shell comprised of a vinyl copolymer having an oxygenic polar group.

According to this invention there is provided the method of producing a core-shell polymer which is defined in claim 1.

In preferred embodiments, the low-gloss polyacetal resin compositions of this invention will include between 1 to 50 parts by weight of the core-shell polymer per 100 parts by weight of the polyacetal base resin.

Further aspects and advantages of this invention will become more clear from the following detailed description of the preferred exemplary embodiments thereof.

The polyacetal base resin that may be used in the compositions of the present invention is a normally solid, high-molecular weight polymer mainly comprised of repeating oxymethylene ($-\text{CH}_2\text{O}-$) units. The polyacetal base resin may be either a polyoxymethylene homopolymer or a copolymer, terpolymer or block copolymer containing a small amount of other monomeric units in addition to oxymethylene units. The polyacetal resin may be linear, branched or crosslinked. Furthermore, the degree of polymerization of the polyacetal resin is not particularly limited.

As briefly noted above, the core-shell polymer according to the present invention includes a rubbery polymer core and a glassy (amorphous) polymer shell comprised of a vinyl copolymer having an oxygenic polar group. The core-shell polymer is produced by a serial multi-stage emulsion polymerization process in which a polymer formed in a first stage in covered with a polymer formed in a final stage. It is preferred that, in the seed particle-forming first stage, the monomer, surfactant and water be fed to the reactor prior to addition to an initiator which initiates the emulsion polymerization reaction.

The first stage polymerization according to the present invention is the stage which forms the rubbery core of the core-shell polymer. In this connection, the monomers that may be employed in the first stage polymerization are selected from conjugated dienes and alkyl acrylates containing 2 to 8 carbon atoms in the alkyl moiety, as well as mixtures thereof. These preferred monomers are thus polymerized in the first stage of the emulsion polymerization process so as to yield the rubbery polymer which will constitute the core of the core-shell polymer.

Specific examples of conjugated dienes that may be employed as the monomer in the first stage polymerization include butadiene, isoprene and chloroprene, with butadiene being particularly preferred. On the other hand, specific examples of alkyl acrylates that can be employed as monomers in the first stage polymerization include ethyl acrylate, propyl acrylate, butyl acrylate, cyclohexyl acrylate and 2-ethylhexyl acrylate. Butyl acrylate, however, is particularly preferred.

Auxiliary comonomers copolymerizable with the conjugated dienes and/or alkyl acrylates can also be employed in the first stage polymerization. Examples of such auxiliary comonomers include various aromatic vinyl or vinylidene compounds (such as styrene, vinyltoluene, α -methylstyrene, and the like), vinyl or vinylidene cyanide compounds (such as acrylonitrile and methacrylonitrile), and alkyl methacrylates (such as methyl methacrylate and butyl methacrylate).

When the first stage polymerization system does not contain a conjugated diene or, if it does but only in a proportion not exceeding 20 wt.% of the total monomer content in the first stage, then improved impact strength proportion can be obtained by incorporating minor (but effective) amounts of a cross-linking monomer and/or a grafting monomer. Examples of suitable cross-linking monomers include, among others, aromatic divinyl monomers such as divinylbenzene, and alkane polyol polyacrylates or polymethacrylates such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, butylene glycol diacrylate, hexanediol diacrylate, hexanediol dimethacrylate, oligoethylene glycol diacrylate, oligoethylene glycol (di)acrylate, tri-methylolpropane dimethacrylate, trimethylolpropane triacrylate and trimethylolpropane trimethacrylate. Particularly preferred are butylene glycol diacrylate and hexanediol diacrylate.

Examples of grafting monomers that may be included in the first stage polymerization system include, among others, allyl esters of unsaturated carboxylic acids, such as allyl acrylate, allyl methacrylate, diallyl maleate, diallyl fumarate and diallyl itaconate. Of these, allyl methacrylate is particularly preferred.

The cross-linking monomer and/or grafting monomer, if used, are present in the first stage polymerization system in an amount up to 5 weight percent, and preferably between 0.1 to 2 weight percent each, based on the total monomer weight.

The shell phase of the core-shell polymer according to the present invention is especially characterized by a glassy (amorphous) polymer comprised of a vinyl copolymer having an oxygenic polar group. In this connection, core-shell polymers which do not have the requisite oxygenic polar group do not impart a sufficient matting (gloss-reducing) effect upon the polyacetal base resin. Likewise, minimal (if any) gloss reduction is achieved when vinyl polymers not having a core-shell structure but having at least one oxygenic polar group are blended with the polyacetal base resin.

The oxygenic polar group is selected from hydroxy, ether ($-\text{O}-$) such as glycidyl, amido ($-\text{CONH}-$), imido ($-\text{CONH}-\text{CO}-$) and nitro ($-\text{NO}_2$) groups. It is preferred to use two or more oxygenic polar groups having an alcohol grouping.

A preferred monomer that may be employed in the final-stage polymerization to form the vinyl polymer having at least one oxygenic polar group may be, for example, a methacrylate or acrylate of an alcohol, said alcohol having two or more oxygenic polar groups, for example, (meth)acrylates of alcohols having hydroxyl groups and/or a glycidyl group. In this connection, specific examples of (meth)acrylates of alcohols having hydroxyl groups include hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate, among which hydroxyethyl methacrylate is preferred. Specific examples of (meth)acrylates of alcohols having a glycidyl group include glycidyl acrylate and glycidyl methacrylate, of which the latter is preferred.

Furthermore, vinyl monomers having an oxygenic polar group other than the (meth)acrylates described above may be employed. For example, allyloxyethanol or allyl glycidyl ether may also be used as a comonomer to form the vinyl polymer forming the shell of the core-shell polymer according to this invention.

The monomers constituting the glassy polymer together with the above-noted monomer having an oxygenic polar group include alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, and the like, aromatic vinyl or vinylidene compounds such as styrene and vinyltoluene α -methylstyrene, and vinyl or vinylidene cyanides such as acrylonitrile and methacrylonitrile. Particularly preferred are methyl methacrylate, styrene and acrylonitrile.

An intermediate phase may be interposed between the first-stage polymer phase and the final-stage polymer phase, if desired. The intermediate phase, if present, can be provided by subjecting a polymerizable monomer having functional groups, such as glycidyl methacrylate, methacrylic acid and hydroxyethyl methacrylate, a polymerizable monomer forming a glassy polymer such as methyl methacrylate, or a polymerizable monomer forming a rubbery polymer, such as butyl acrylate, to polymerization conditions in an intermediate emulsion polymerization stage.

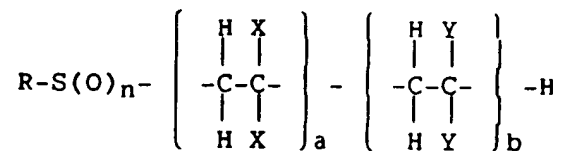
A variety of intermediate phase morphologies can be selected according to the proportion that are desired for the resulting core-shell polymer. In this regard, the core-shell polymer having such an intermediate phase may, for example, be a multilayer system in which the intermediate phase is interposed as a layer between the core and shell polymers, or as a "salami-like" system in which the intermediate phase is dispersed as small particles throughout the core polymer. In this latter morphology, the intermediate phase may form a new subcore in the centre of the core polymer as is sometimes the case when styrene is used as the intermediate phase-forming monomer.

The use of a core-shell polymer having an intermediate phase may result in improvements in the impact strength and heat-distortion temperature, as well as enhancements in the flexural modulus. In addition, improved appearance characteristics of the core-shell polymer as a result of the presence of the intermediate phase may result due to decreased molding delamination and reduced pearlescence and color variations because of refractive index changes in the resulting molded articles.

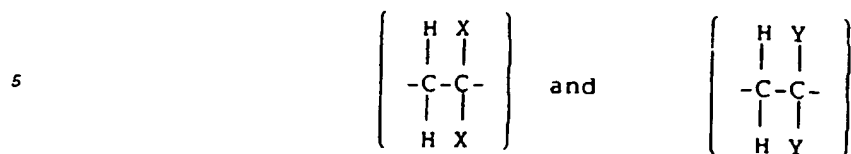
The emulsion polymerization according to the present invention is carried out using a surfactant, such as a nonionic surfactant or an oligomeric anionic or nonionic surface, as well as a polymerization initiator, such as an azo or peroxide polymerization initiator.

A number of well known surfactants that are commonly used in emulsion polymerization processes generally can also be employed in the emulsion polymerization process according to this invention. Thus, for example, there may be employed nonionic ether type surfactants such as polyoxyethylene nonylphenyl ether, polyoxyethylene stearyl ether and polyoxyethylene lauryl ether; nonionic ester type surfactants such as polyoxyethylene monostearate; nonionic sorbitan ester type surfactants, such as polyoxyethylene sorbitan monolaurate; and nonionic block copolymer type surfactants such as polyoxyethylene polyoxypropylene block copolymers.

The preferred surfactants to be used in the processes of this invention, however, are oligomeric anionic or nonionic surfactants such as those which have been used in emulsion polymerization reactions for certain specialized purposes. For example, oligomeric surfactants of the following formula (and which are described in Japanese Patent Publication Nos. 34832/1972, 34833/1972 and 38080/1972) can be employed in the emulsion polymerization process of this invention:



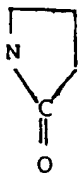
wherein the structural units represented by the formulae:



are randomly arranged in the surfactant's molecule, and wherein R represents an alkyl group of 5 to 20 carbon atoms, preferably 6 to 12 carbon atoms; n is 0, 1 or 2, and preferably 0 or 1, and more preferably 0; R_1 and R^3 , which may be the same or different, represent -H, -CH₃, -C₂H₅, or -COOH; R_2 and R_4 , which may be the same or different, represent -H, -CH₃, -C₂H₅, -COOH or -CH₂COOH; X represents -COOH, -CONH₂, -OCH₃ or -OC₂H₅; and Y represents -CH₂OH,

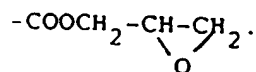
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-CONH₂, -COOC₂H₄OH, -CONHCH₂OH, -CONHCH₃, -CONHC₂H₅, -CONHC₃H₇, -COOHCH₃, -COOC₂H₅, -CN, -OCOCH₃, -OCOC₂H₅, or

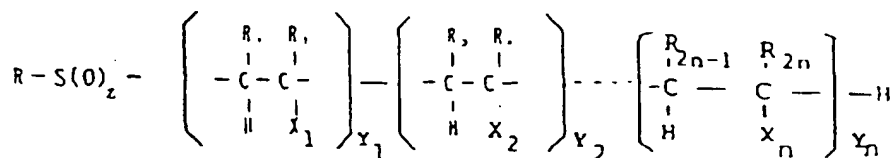
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In other words, the surfactant may be defined by

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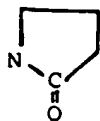


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In the above formula, R means an alkyl group of 5 to 20 carbon atoms, preferably 6 to 12 carbon atoms. Z is equal to 0, 1 or 2; preferably 0 or 1, and more preferably 0; n is an integral number of 2 or more; R_{2n-1} respectively represents -H, -CH₃, -C₂H₅ or -COOH; R_{2n} respectively represents -H, -CH₃, -C₂H₅, -COOH or -CH₂COOH; X represents -COOH, -CONH₂, OCH₃, -OC₂H₅, -CH₂OH,

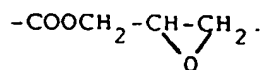
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-CONH₂, -COOC₂H₄OH, -COOC₃H₆OH, -CONHCH₂OH, -CONHCH₃, -CONHC₂H₅, -CONHC₃H₇, -COOCH₃, -COOC₂H₅, -CN, -OCOCH₃, -OCOC₂H₅, or

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The molecular weight of the oligomeric surfactant to be used in accordance with the invention is 200 to 5000, preferably 1500 to 3000, with the degree of polymerization

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$$\left(\sum_{a=1}^n Y_a \right)$$

ranging from 6 to 50.

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The oligomeric surfactant as such may be water-soluble. However, if the surfactant is not water-soluble, then it is converted to a water-soluble salt by reacting the non-water-soluble precursor with an oxide, hydroxide or alcohol. The water-soluble salt may include, among others, alkali metal salts, alkaline earth metal salts, Group III heavy metal salts, ammonium salt and substituted ammonium salts. Ammonium salts are particularly preferred.

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The proportion of the oligomeric surfactant that is employed in the practice of this invention is selected with reference to the particle stabilizing power of the particular surfactant that is used.

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The oligomeric surfactants can be synthesized, for example according to the techniques described in Japanese Patent Publication No. 47-34832, by the addition polymerization of relevant monomers in an anhydrous solvent in the presence of an alkyl mercaptan and, if necessary, oxidizing the oligomer with hydrogen peroxide or ozone to the corresponding sulfoxide or sulphone. The alkyl mercaptan may include, among others, n-octyl mercaptan, n-dodecyl mercaptan, t-dodecylmercaptan and n-decyl mercaptan. The addition polymerization is typically carried out in the temperature range of 20 to 100°C.

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The monomers mentioned above include α,β -ethylenically unsaturated monomers having at least one polar group, such as (meth)acrylic acid, α -ethyl acrylate, β -methyl acrylate, α,β -dimethyl acrylate, caproic acid, itaconic acid, fumaric acid, maleic acid, (meth)acrylamide, vinyl ethyl ether, vinyl methyl ether, allyl alcohol, vinylpyrrolidone, (meth)acrylonitrile, ethylacrylonitrile, methyl (meth)acrylate, ethyl acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, vinyl acetate, vinyl propionate, N-isopropylacrylamide, N-ethylacrylamide, N-methylacrylamide, glycidyl (meth)acrylate and N-methylolacrylamide.

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The solvent that is used during the addition polymerization is preferably a lower alkanol, such as methanol, ethanol and isopropyl alcohol.

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As noted briefly above, azo type initiators, such as azobis(isobutyronitrile), dimethyl 2,2'-azobis(isobutyrate), 2,2'-azobis(2-amidinopropane) dihydrochloride, and peroxides, such as cumene hydroperoxide, diisopropylbenzene hydroperoxide, hydrogen peroxide can be employed successfully. These specific initiators may be used alone or in combination.

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The emulsion polymerization in a reaction system containing the nonionic surfactant and/or oligomeric surfactant, and an azo and/or a peroxide initiator yields a core-shell polymer which includes minimal (if any) sulphur-containing anions. If present, the content of sulphur-containing anions (such as sulphate or sulphate ester ions) in the core-shell polymer according to the present invention is so low as not to be detected by the following conventional qualitative tests for sulphur-containing anions. Since the core-shell polymer according to the present invention is substantially free from sulphur-containing anions, it can homogeneously be melt-blended with polyacetal resin without detrimentally affecting the polyacetal resin's properties so as to produce polyacetal-based resin compositions which exhibit excellent surface-dullness, impact resistance, and elongation.

The sulphur-containing anion includes sulphur oxide compounds, such as sulphate, persulphate, sulphite and sulphonate.

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The presence of sulphur-containing anions in a core-shell polymer can be determined by a qualitative test procedure which includes weighing 5 g of a core-shell polymer sample and placing it in a 50 ml Erlenmeyer flask to which 20 ml of deionized water is added. The contents of the flask are stirred with a magnetic stirrer for 3 hours, after which the contents are filtered through a No. 5 filter paper. The Filtrate is divided into two portions. 0.5 ml of a 1% aqueous solution of barium chloride is added to one of the portions and the turbidity of the resulting mixture is compared with that of the other filtrate portion.

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The core-shell polymer according to the present invention can be in the form of granules, flakes or powders, for example, by producing a latex of the core-shell polymer using the above-described emulsion polymerization process in the presence of a surfactant and initiator. The latex is then subjected to a freeze-thaw cycle so as to separate the polymer, followed by centrifugally dehydrating the polymer and final drying. The solvent and the surfactant used in the emulsion polymerization process can thus substantially be removed from the core-shell polymer.

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Alternatively, the latex may be dried and used in its as-produced form, instead of being subjected to a freeze-thaw cycle described above. In this connection, spray-drying using a spray drier can also be utilized for recovery of the core-shell polymer from the latex.

The core-shell polymer thus isolated and recovered may then be processed into pellets by means of an extruder

or pelletizer. Alternatively, the recovered core-shell polymer may be directly melt-blended with a matrix resin to achieve improved impact strength properties, for example, for the resulting melt-blended composition.

The core-shell polymer described above is present in the composition of the present invention in an amount of 1 to 50 parts by weight, preferably 1 to 20 parts by weight, per 100 parts by weight of the polyacetal base resin. If the amount of the core-shell polymer is too small, insufficient reduction of the surface gloss will ensue. On the other hand, if the amount of the core-shell polymer is excessive, the mechanical properties, particularly stiffness, will be adversely affected. In addition, excessive amounts of the core-shell polymer will impart detrimental effects upon the compositions' heat stability characteristics.

Molded articles formed from the polyacetal compositions of this invention not only exhibit uniformly lower surface gloss and high-grade appearance characteristics, but also retain the excellent mechanical properties that are inherent in polyacetal resin. The reasons why these effects are obtained are not fully understood at this time. However, without wishing to be bound to any particular theory, it is surmised that the core-shell polymer is dispersed in the surface region of the molded article in the form of particles having a size between 0.5 to 2.0 μm . As a result, the surface of the article is roughened by the presence of these core-shell polymer particles. In addition, the oxygenic polar groups are uniformly dispersed on the surface of the article so that its surface appearance is modified resulting in lower surface gloss.

The compositions of this invention typically exhibit a surface gloss of 35% or less, and more typically 25% or less, as determined at a reflection angle of 45°-45° according to JIS K 7105.

It is desirable that the compositions of this invention includes known heat stabilizers so as to improve the heat stability of the resulting composition. In this connection, it is desirable to use one or more stabilizers selected from among known antioxidants, nitrogen compounds, and alkali or alkaline earth metal compounds.

In addition, the compositions of the present invention may suitably be colored by the incorporation of various carbon blacks or other dyes and/or pigments conventionally employed in the field of engineering resins. Furthermore, virtually any other additive employed in engineering resins conventionally may be incorporated into the compositions of the present invention no as to achieve desired property characteristics.

The compositions of the present invention can be prepared by conventional processes for preparing synthetic resin compositions using conventional processing equipment. For example, the necessary components may be mixed together, kneaded and extruded with a single- or twin-screw extruder to provide pellets, followed by molding of the pellets to form articles. Alternatively, the composition may be prepared by adding all components to a molding machine so that melt-blending occurs simultaneously with molding to form articles. Further, a part or the entirety of the resin components may be pulverized and mixed with the residual components, followed by melt-extrusion to provide pellets. The pellets may then be employed to form molded articles. The above-noted optional stabilizers and additives may arbitrarily be added in any process step prior to the production of a final molded article.

The polyacetal compositions of the present invention exhibit significantly improved effects in terms of lowering the surface gloss characteristics for molded articles formed of the compositions by virtue of the presence of the core-shell polymer, without detrimentally affecting the inherent physical and mechanical properties that are attributable to the polyacetal base resin. The compositions are also improved in mechanical properties and thermal stability. Accordingly, molded articles having satisfactory physical and mechanical properties can be provided with "engineered" surface gloss characteristics.

The compositions of the invention are molded in a conventional manner such as injection, extrusion and compression or pressing, preferably at a temperature of 180 to 240°C. The resultant molded articles are useful for automobile interior trim parts, optical instruments and electric appliances.

The invention is further illustrated by the following non-limiting examples.

EXAMPLES

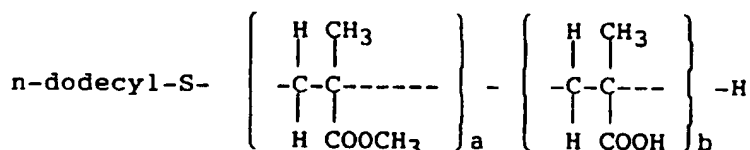
In the following Examples, all components are expressed in parts by weight, and the following abbreviations have been used:

| Component | Abbreviation |
|---|--------------|
| ethyl acrylate | EA |
| methyl methacrylate | MMA |
| butyl acrylate | BA |
| 1,4-butylene glycol diacrylate | BGA |
| allyl methacrylate | AIMA |
| methacrylamide | MAM |
| nonionic surfactant (polyoxyethylene nonylphenyl ether, Emulgen 950, Kao Corporation) | E950 |

(continued)

| Component | Abbreviation |
|---|--------------|
| deionized water | DIW |
| 2,2'-azobis(2-amidinopropane) | V50 |
| dihydrochloride (V50, Wako Pure Chemical Industries Ltd.) | V50 |
| 2-hydroxyethyl methacrylate | HEMA |
| styrene | St |
| glycidyl methacrylate | GMA |
| polyacetal resin | POM |
| oligomeric anionic surfactant | Surfactant A |

The oligomeric anionic surfactant designated "Surfactant A" had the following formula and was synthesized as in Example 13 of Japanese Kokai Patent Application No. 53-10682, adjusted to pH 7.5 with aqueous ammonia and diluted with purified water to make a solid content of 10%:



(wherein $a : b = 7 : 3$, $a + b = 13.6$, and molecular weight = 1310)

| Composition | Amount |
|-------------------|--------|
| methacrylic acid | 155 g |
| MMA | 360 g |
| n-DMP | 109 g |
| AIBN | 4.4 g |
| isopropyl alcohol | 314 g |

Example 1 - Production of Core-shell Polymer A

1200 g of DIW, 1.68 g of 25% aqueous ammonia, 7 g of surfactant A and 0.14 g of MAM were charged into a 5 litre polymerization reactor equipped with a reflux condenser. The reactor charge was heated to 70°C under a stream of nitrogen while being stirred. 27.86 g of a seed monomer mixture of the following composition was then added and dispersed over 10 minutes, followed by the addition of 21 g of a 10% aqueous solution of V50 to initiate seeded polymerization:

| Seed Monomers | Amount |
|---------------|----------|
| EA | 27.664 g |
| AIMA | 0.14 g |
| BGA | 0.056 g |

After 7 g of MAM were added, a monomer emulsion prepared by adding 210 g of surfactant A, 900 g of DIW and 2.80 g of 25% aqueous ammonia to 1365 g of a core monomer mixture of the following composition and a mixture of 21.0 g of a 10% aqueous solution of V50 and 0.63 g of 1% aqueous ammonia were continuously fed over a period of 180 minutes for further seeded polymerization:

EP 0 494 534 B1

| Core Monomer Mixture: | |
|-----------------------|----------|
| Component | Amount |
| BA | 1215.2 g |
| MMA | 140.0 g |
| BGA | 2.8 g |
| AIMA | 7.0 g |

The reaction mixture was heated to 80°C, aged for one hour and cooled to 70°C, after which, 9 g of a 10% aqueous solution of VSO and 0.27 g of 1% aqueous ammonia were added to the reactor. A shell monomer emulsion of the following composition, 12 g of a 10% aqueous solution of VSO and 0.36 g of 1% aqueous ammonia were continuously fed thereto over 60 minutes for further seeded polymerization:

| Shell Monomer Emulsion | |
|------------------------|---------|
| Component | Amount |
| MMA | 265.8 g |
| EA | 60.0 g |
| Surfactant A | 30.0 g |
| DIW | 500.0 g |
| 25% aqueous ammonia | 0.72 g |
| St | 180.0 g |
| HEMA | 90.0 g |
| BGA | 1.2 g |
| MAM | 3.0 g |

The reaction mixture was heated to 80°C, aged for one hour, cooled, and filtered through a 300-mesh (48 µm) stainless steel screen to yield a core-shell polymer latex. The latex was frozen at -15°C, thawed to room temperature and filtered through a glass filter. The filter cake was dried in an air current at 60°C for 24 hours to give the core-shell polymer A.

Examples 2 to 4 - Production of Core-Shell Polymers B to D, Respectively

Polymerization was carried out in the same manner as that of Example 1 above, except that each monomer mixture was the composition specified in the following Table 1. Also in these examples, 35 g of the core monomer mixture was used as the seed monomers. The results of these examples were that core-shell polymers B to D were obtained.

Table 1

| | Monomer composition (pts. by wt.) | Core-shell polymer (symbol) | | |
|-------|-----------------------------------|-----------------------------|--------|--------|
| | | B | C | D |
| Core | BA | 1243.2 | 1243.2 | 1250.2 |
| | MMA | 140.0 | 140.0 | 140.0 |
| | BGA | 2.8 | 2.8 | 2.8 |
| | AIMA | 14.0 | 14.0 | 7.0 |
| Shell | MMA | 448.8 | 508.8 | 478.8 |
| | EA | 60.0 | 60.0 | 60.0 |
| | GMA | - | - | 60.0 |
| | HEMA | 90.0 | 30.0 | - |
| | BGA | 1.2 | 1.2 | 1.2 |

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Examples 5 to 13 - Production of POM Resin Compositions (1) to (9)

A POM copolymer resin (a product of Polyplastics Co., Ltd., trade-name Duracon) and each of the core-shell polymers A to D produced above were dried until the water content had been reduced to 0.3%. These components were then melt-blended with one another at a ratio specified in Table 2 below using a twin-screw extruder PCM-30 manufactured by Ikegai Corporation at a cylinder temperature of 200°C and a die head temperature of 200°C to form pelletized POM compositions (1) to (9).

Comparative Example 1 - Production of POM Resin Composition (10)

A POM copolymer resin and an Impact modifier E (a product of Rohm & Haas: KM330) were melt-kneaded together at a ratio specified in Table 3 to obtain pelletized POM resin composition (10).

Comparative Example 1 - Production of Core-Shell Polymer F

1320 g of DIW and 66 g of a 10% aqueous solution of E950 were charged into a 5 liter polymerization reactor equipped with a reflux condenser, with the charge being stirred and heated to 70°C under a nitrogen stream. 77 g of a core monomer mixture of the following composition were added and dispersed over 10 minutes, followed by addition of 154 g of a 2% aqueous solution of V50 to initiate a seeded polymerization.

| Core Monomer Mixture: | |
|-----------------------|-----------|
| Component | Amount |
| EA | 1533.84 g |
| AIMA | 3.08 g |
| BGA | 3.08 g |

A monomer emulsion was then prepared by adding 440 g of a 10% aqueous solution of E950 and 440 g of DIW to the remainder (1463 g) of the core monomer mixture was continuously fed over 180 minutes for further seeded polymerization.

The reaction mixture was aged at a temperature of 70°C for one hour and transferred to the second polymerization stage.

In the second polymerization stage 66 g of a 2% aqueous solution of V50 was added to the reactor and 1120 g of a shell monomer emulsion of the following composition was continuously fed over 60 minutes for further seeded polymerization:

| Shell Monomer Emulsion: | |
|---------------------------|---------|
| Component | Amount |
| MMA | 594.0 g |
| EA | 66.0 g |
| 10% aqueous solution E950 | 220.0 g |
| DIW | 440.0 g |

The reaction mixture was heated to 80°C, aged for one hour, cooled and filtered through a 300-mesh (48 µm) stainless steel screen to give a core-shell polymer latex.

This polymer latex was frozen at -15°C, thawed to room temperature and filtered through a glass filter. The filter cake was dried in an air current at 60°C to yield the core-shell polymer F.

Comparative Examples 3 and 4 - Production of POM Resin Compositions (11) and (12)

Pelletized POM resin compositions (11) and (12) were produced by using the core-shell polymer F in a similar manner to that described above for the preparation of POM composition (1). The formulation of each composition is given in Table 3.

Comparative Examples 5 and 6 - Production of Acrylic Resins G and H

A monomer mixture of the following composition was solution-polymerized randomly in toluene at 70°C using AIBN as a polymerization initiator (in an amount of 0.1% by weight based on the monomer mixture). The formed polymer was precipitated in a poor solvent and dried to obtain acrylic resins G and H having the following comonomer contents:

Acrylic Resin G : MMA/H EMA = 80/20

Acrylic Resin H: MMA/GMA = 80/20

Comparative Examples 7 to 10 - Production of POM Resin Compositions (13) to (16)

Pelletized POM resin compositions (13) to (16) were produced by using the core-shell polymer F and acrylic resins G and H prepared in Comparative Examples 2,5 and 6 in a similar manner to that used to prepared POM composition (1). The formulations of each composition is given in Table 3.

Qualitative Test for Sulphate Ions

The sulphate ions in the core-shell polymers A to D, F and the impact modifier E were determined by the following procedure. 5 g of each sample were weighed into a 50 ml conical flask to which 20 ml of DIW was added. The mixture was then stirred with a magnetic stirrer for 3 hours. The stirred mixture was filtered through a No. 5C filter paper with the filtrate thereafter being divided into two substantially equal portions. 0.5 ml of a 1% aqueous solution of barium chloride was added to one of the portions and the relative turbidity of the two portions was then qualitatively observed.

According to this test, no sulphate ions were detected in the core-shell polymers A to D and F, but sulphate ions were detected in the impact modifier E.

Evaluation of Physical Characteristics

The POM resin compositions (1) to (17) produced in the manner described above and a control resin composition which did not contain any impact modifier were each examined for various physical characteristics according to the following procedures. The results appear in Tables 2 and 3.

(1) Determination of Surface Appearance and Surface Gloss Characteristics

A test piece (70mm x 40mm x 30mm) prepared by molding each composition under the following conditions was examined for surface appearance and surface gloss characteristics:

Molding Machine: Toshiba Corporation, IS 80

Molding Conditions:

| | nozzle | C1 | C2 | C3 |
|---------------------|----------------------------------|-----|-----|-----|
| cylinder temp. (°C) | 200 | 190 | 180 | 160 |
| injection pressure | 64 MPa (650 kg/cm ²) | | | |
| injection speed | 1.0 m/min | | | |
| mold temp. (°C) | 80 | | | |

(i) Surface Appearance: The surface appearance was evaluated in terms of dullness and surface uniformity and classified subjectively into the following four ranks, whereby the lesser ranking means better dullness and higher uniformity.

Rank

1 The surface is uniformly rough and no outline of a fluorescent illuminating lamp is visible on the surface.

2 The surface is non-uniformly rough, but no outline of the illuminating lamp is observed.

3 An obscure outline of the lamp is perceptible.

4 A clear outline of the lamp is perceptible, and the surface is nearly smooth.

5 (ii) Surface Gloss: The surface gloss was determined at a reflection of 45°-45° according to JIS K 7105 using a digital glossmeter of the variable angle type manufactured by Suga Test Instruments Co., Ltd., UGV-40.

(2) Tensile-Test

10 The tensile strength and elongation of the specimens were determined according to ASTM D638.

(3) Izod Impact Strength (Notched)

Notched Izod impact strength data was obtained using the procedures of ASTM D256

Note to Table 3

15 POM resin composition (10) failed during molding, presumably owing to bubbling during the extrusion caused by the decomposition of polyoxymethylene, and as a result, the surface appearance was not evaluated.

20 While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

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TABLE 2

| (Example) | | POM resin composition No. | | | | | | | | |
|---------------------------------|--------------------------------|---------------------------|------|-----|------|------|-----|------|------|-----|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| POM resin (pts. by wt.) | | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Core-shell polymer | symbol | A | B | B | B | B | C | C | C | D |
| | (pts. by wt.) | 10 | 5 | 10 | 20 | 30 | 5 | 10 | 20 | 10 |
| Acrylic resin | symbol | | | | | | | | | |
| | (pts. by wt.) | | | | | | | | | |
| Surface appearance | | 1 | 2 | 1 | 1 | 1 | 2 | 1 | 1 | 1 |
| Tensile test | Gloss (45° - 45°)(%) | 15 | 23 | 14 | 10 | 8.5 | 27 | 22 | 14 | 21 |
| | elongation (%) | 79 | 78 | 96 | 104 | 121 | 87 | 105 | 126 | 84 |
| | strength (kg/cm ²) | 622 | 530 | 490 | 475 | 459 | 531 | 490 | 455 | 520 |
| Isod impact strength (kg·cm/cm) | | 7.8 | 10.0 | 9.0 | 11.2 | 14.9 | 9.1 | 10.0 | 12.5 | 8.5 |

TABLE 3

| (Comparative Example) | | POM resin composition No. | | | | | | | | | |
|---------------------------------|--------------------------------|---------------------------|------|------|-----|-----|-----|-----|-----|---------|--|
| | | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | control | |
| POM resin (pts. by wt.) | | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | |
| Core-shell polymer | symbol | B | P | P | | | | P | | | |
| | (pts. by wt.) | 10 | 10 | 20 | | | | 10 | | | |
| Calcium carbonate | | | | | | | | | 20 | | |
| Acrylic resin | symbol | | | | G | G | H | O | | | |
| | (pts. by wt.) | | | | 10 | 20 | 10 | 10 | | | |
| Surface appearance | | (*) | 4 | 3 | 4 | 3 | 4 | 4 | 2 | 4 | |
| Gloss (45° - 45°)(%) | (mirror surface) | - | 85 | 48 | 52 | 37 | 55 | 57 | 27 | 79 | |
| | elongation (%) | - | 101 | 129 | 35 | 22 | 24 | 57 | 21 | 58 | |
| Tensile test | | | | | | | | | | | |
| | strength (kg/cm ²) | - | 494 | 470 | 574 | 585 | 573 | 528 | 516 | 580 | |
| Izod impact strength (kg·cm/cm) | | - | 11.0 | 13.8 | 9.3 | 2.9 | 3.1 | 6.2 | 3.4 | 5.5 | |

Claims

1. A method of producing a core-shell polymer having as the core a rubbery polymer and as the shell a glassy vinyl copolymer with at least one oxygenic group, characterised by a serial multi-stage emulsion polymerisation process which comprises the steps of:
 - (a) subjecting in a first stage a reaction mixture which includes at least one monomer selected from conjugated dienes and alkyl acrylates containing 2 to 8 carbon atoms in the alkyl moiety, an oligomeric surfactant and/or a nonionic surfactant and an initiator to emulsion polymerization conditions for a time sufficient to form said rubbery polymer;
 - (b) introducing the rubbery polymer formed in said first stage into a final stage reaction mixture which includes said rubbery polymer; a vinyl monomer having at least one oxygenic polar group selected from hydroxy, ether (-O-) such as glycidyl, amido (-CONH-), imido (-CONHCO-) and nitro (-NO₂) groups; an oligomeric surfactant and/or a nonionic surfactant; and an initiator; and
 - (c) subjecting the final stage reaction mixture to emulsion polymerization conditions sufficient to form, over a core of the rubbery polymer, a glassy vinyl copolymer shell having an oxygenic group.
2. A method as claimed in claim 1, wherein the monomer in the first stage polymerization is selected from butadiene, isoprene, chloroprene, ethyl acrylate, propyl acrylate, butyl acrylate, cyclohexyl acrylate and 2-ethylhexyl acrylate.
3. A method as claimed in claim 1 or claim 2, wherein an auxiliary comonomer copolymerizable with the conjugated dienes and/or alkyl acrylates is also employed in the first stage polymerization.
4. A method as claimed in any preceding claim, wherein the initiator used in the first and final stages is at least one selected from azo and peroxide emulsion polymerization initiators.
5. A method as claimed in any preceding claim, wherein the or each oxygenic polar group is a hydroxyl or glycidyl group.
6. A method as claimed in any preceding claim, wherein the vinyl monomer is an acrylate or methacrylate of an alcohol, said alcohol having two or more oxygenic polar groups.
7. A method as claimed in claim 5 or 6, wherein the glassy vinyl copolymer is formed from one or more vinyl monomers selected from: hydroxyethyl (meth)acrylate; hydroxypropyl (meth)acrylate; glycidyl (meth)acrylate; allyloxyethanol; allyl glycidyl ether; together with a comonomer being one or more of: methyl (meth)acrylate; ethyl (meth)acrylate; butyl (meth)acrylate; aromatic vinyl or vinylidene compounds such as vinyltoluene α -methylstyrene and styrene; vinyl or vinylidene cyanides such as acrylonitrile and methacrylonitrile.
8. A method as claimed in claim 7, wherein the vinyl monomer is hydroxyethyl methacrylate or glycidyl methacrylate.
9. A method as claimed in claim 7 or 8, wherein the comonomer is methyl methacrylate, styrene, or acrylonitrile.
10. A resin composition comprising a polyacetal base resin together with a core-shell polymer produced by a method as claimed in any preceding claim, wherein the core-shell polymer is present in an amount between 1 and 50 parts by weight per 100 parts by weight of the base resin and is in the form of particles having a size from 0.5 to 2.0 μ m.
11. A resin composition as claimed in claim 10, comprising a polyacetal base resin and a core-shell polymer having as the core a rubbery polymer and as the shell a glassy vinyl copolymer with at least one oxygenic polar group, which resin and core-shell polymer have been melt blended to form a low surface-gloss moldable polyacetal resin composition.
12. A composition as claimed in claim 10 or 11, wherein the base resin is a polyacetal homopolymer or copolymer.
13. A low surface-gloss molded polyacetal resin article which comprises a polyacetal resin composition as claimed in any of claims 10 to 12.

Patentansprüche

1. Verfahren zur Herstellung eines Kern-Schale-Polymers mit einem kautschukartigen Polymer als Kern und einem glasartigen Vinyl-Copolymer mit wenigstens einer sauerstoffhaltigen Gruppe als Schale, gekennzeichnet durch ein serielles Mehrstufen-Emulsions-Polymerisationsverfahren, umfassend die Schritte des:
 - (a) Unterwerfens einer Reaktionsmischung, die wenigstens ein Monomer, ausgewählt aus 2 bis 8 Kohlenstoffatome im Alkylrest enthaltenden konjugierten Dienen und Alkylacrylaten, ein oligomeres Tensid und/oder ein nichtionisches Tensid und einen Initiator umfaßt, in einer ersten Stufe Emulsions-Polymerisationsbedingungen für einen Zeitraum, der zur Bildung des kautschukartigen Polymers ausreichend ist;
 - (b) Einführens des in der ersten Stufe gebildeten kautschukartigen Polymers in eine Endstufen-Reaktionsmischung, die das kautschukartige Polymer, ein Vinylpolymer mit wenigstens einer sauerstoffhaltigen polaren Gruppe, ausgewählt aus Hydroxy-, Ether(-O-) wie Glycidyl-, Amido- (-CONH-), Imido-(-CONHCO-) und Nitro-(-NO₂) Gruppen; ein oligomeres Tensid und/oder ein nichtionisches Tensid und einen Initiator umfaßt; und
 - (c) Unterwerfens der Endstufen-Reaktionsmischung Bedingungen der Emulsions-Polymerisation, die ausreichend sind, um über einem Kern des kautschukartigen Polymers eine Schale aus glasartigem Vinyl-Copolymer zu bilden, das eine sauerstoffhaltige Gruppe aufweist.
2. Verfahren nach Anspruch 1, wobei das Monomer für die Erststufen-Polymerisation aus Butadien, Isopren, Chloropren, Ethylacrylat, Propylacrylat, Butylacrylat, Cyclohexylacrylat und 2-Ethylhexylacrylat ausgewählt ist.
3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei ein Zusatz-Comonomer, das mit den konjugierten Dienen und/oder Alkylacrylaten copolymerisierbar ist, ebenfalls bei der Erststufen-Polymerisation eingesetzt wird.
4. Verfahren nach einem der vorhergehenden Ansprüche, wobei es sich bei dem für die erste und letzte Stufe verwendeten Initiator wenigstens um einen aus Azo und Peroxid ausgewählten Initiator für die Emulsions-Polymerisation handelt.
5. Verfahren nach einem der vorhergehenden Ansprüche, wobei es sich bei der oder jeder sauerstoffhaltigen Gruppe um eine Hydroxyl- oder Glycidylgruppe handelt.
6. Verfahren nach einem der vorhergehenden Ansprüche, wobei es sich beim Vinylmonomer um ein Acrylat oder Methacrylat eines Alkohols handelt, wobei der Alkohol zwei oder mehr sauerstoffhaltige polare Gruppen aufweist.
7. Verfahren nach Anspruch 5 oder 6, wobei das glasartige Vinyl-Copolymer aus einem oder mehr Vinylmonomeren gebildet wird, ausgewählt aus: Hydroxyethyl(meth)acrylat; Hydroxypropyl(meth)acrylat; Glycidyl(meth)acrylat; Allyloxyethanol; Allylglycidylether; zusammen mit einem Comonomer, wobei es sich um eines oder mehrere von: Methyl(meth)acrylat; Ethyl(meth)acrylat; Butyl(meth)acrylat; aromatische Vinyl- oder Vinylidenverbindungen wie Vinyltoluol- α -methylstyrol und Styrol; Vinyl- oder Vinylidencyanide wie Acrylnitril und Methacrylnitril handelt.
8. Verfahren nach Anspruch 7, wobei es sich beim Vinylmonomer um Hydroxyethylmethacrylat oder Glycidylmethacrylat handelt.
9. Verfahren nach Anspruch 7 oder 8, wobei es sich beim Comonomer um Methylmethacrylat, Styrol oder Acrylnitril handelt.
10. Harzzusammensetzung, umfassend ein Polyacetal-Grundharz zusammen mit einem Kern-Schale-Polymer, hergestellt durch ein Verfahren nach einem der vorhergehenden Ansprüche, wobei das Kern-Schale-Polymer in einer Menge zwischen 1 und 50 Gewichtsteilen auf 100 Gewichtsteile des Grundharzes vorhanden ist und in Form von Teilchen mit einer Größe von 0,5 bis 2,0 μ m vorliegt.
11. Harzzusammensetzung nach Anspruch 10, umfassend ein Polyacetal-Grundharz und ein Kern-Schale-Polymer, das als Kern ein kautschukartiges Polymer und als Schale ein glasartiges Vinylpolymer mit wenigstens einer sauerstoffhaltigen polaren Gruppe aufweist, wobei das Harz und das Kern-Schale-Polymer schmelzvermischt worden sind, so daß eine formpreßbare Polyacetal-Harzzusammensetzung mit niedrigem Oberflächenglanz gebildet wird.

12. Zusammensetzung nach Anspruch 10 oder 11, wobei es sich beim Grundharz um ein Polyacetal-Homopolymer oder -Copolymer handelt.

5 13. Formgepreßter Gegenstand aus Polyacetalharz mit niedrigem Oberflächenglanz, umfassend eine Polyacetal-Zusammensetzung nach einem der Ansprüche 10 bis 12.

Revendications

10 1. Procédé de préparation d'un polymère coeur-enveloppe ayant en tant que coeur un polymère caoutchouteux et en tant qu'enveloppe un copolymère vinylique vitreux ayant au moins un groupe oxygéné, caractérisé par un procédé de polymérisation en émulsion à plusieurs stades en série qui comprend les étapes consistant à :

15 (a) soumettre, dans un premier stade, un mélange réactionnel qui inclut au moins un monomère choisi parmi les diènes conjugués et les acrylates d'alkyle contenant 2 à 8 atomes de carbone dans la partie alkyle, un agent tensioactif oligomère et/ou un agent tensioactif non ionique et un initiateur, à des conditions de polymérisation en émulsion pendant une durée suffisante pour former ledit polymère caoutchouteux ;

20 (b) introduire le polymère caoutchouteux formé dans ledit premier stade dans un mélange réactionnel de stade final qui inclut ledit polymère caoutchouteux ; un monomère vinylique ayant au moins un groupe polaire oxygéné choisi parmi les groupes hydroxy, éther (-O-) tel que le groupe glycidyle, amido (-CONH-), imido (-CONHCO-) et nitro (-NO₂) ; un agent tensioactif oligomère et/ou un agent tensioactif non ionique ; et un initiateur ; et à

25 (c) soumettre le mélange réactionnel de stade final à des conditions de polymérisation en émulsion suffisantes pour former, sur un coeur du polymère caoutchouteux, une enveloppe en copolymère vinylique vitreux ayant un groupe oxygéné.

2 2. Procédé selon la revendication 1, dans lequel le monomère dans la polymérisation du premier stade est choisi parmi le butadiène, l'isoprène, le chloroprène, l'acrylate d'éthyle, l'acrylate de propyle, l'acrylate de butyle, l'acrylate de cyclohexyle et l'acrylate de 2-éthylhexyle.

30 3. Procédé selon la revendication 1 ou la revendication 2, dans lequel un comonomère auxiliaire copolymérisable avec les diènes conjugués et/ou acrylates d'alkyle est aussi employé dans la polymérisation du premier stade.

35 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'initiateur utilisé dans le premier stade et le stade final est au moins un initiateur choisi parmi les initiateurs de polymérisation en émulsion azoïques et peroxydes.

40 5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le ou chaque groupe polaire oxygéné est un groupe hydroxyle ou glycidyle.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le monomère vinylique est un acrylate ou un méthacrylate d'un alcool, ledit alcool ayant deux groupes polaires oxygénés ou plus.

45 7. Procédé selon la revendication 5 ou 6, dans lequel le copolymère vinylique vitreux est formé à partir d'un ou plusieurs monomères vinyliques choisis parmi : le (méth)acrylate d'hydroxyéthyle ; le (méth)acrylate d'hydroxypropyle ; le (méth)acrylate de glycidyle ; l'allyloxyéthanol ; l'éther d'allyle et de glycidyle ; avec un comonomère qui est un ou plusieurs des suivants : le (méth)acrylate de méthyle ; le (méth)acrylate d'éthyle ; le (méth)acrylate de butyle ; les composés de vinyle ou de vinylidène aromatiques tels que le vinyltoluène, le α -méthylstyrène et le styrène ; les cyanures de vinyle ou de vinylidène tels que l'acrylonitrile et le méthacrylonitrile.

50 8. Procédé selon la revendication 7, dans lequel le monomère vinylique est le méthacrylate d'hydroxyéthyle ou le méthacrylate de glycidyle.

55 9. Procédé selon la revendication 7 ou 8, dans lequel le comonomère est le méthacrylate de méthyle, le styrène ou l'acrylonitrile.

10. Composition de résine comprenant une résine de base de polyacétal avec un polymère coeur-enveloppe préparé par un procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans laquelle le poly-

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mère coeur-enveloppe est présent en une quantité comprise entre 1 et 50 parties en poids pour 100 parties en poids de la résine de base et est sous la forme de particules ayant une taille de 0,5 à 2,0 μm .

- 5 11. Composition de résine selon la revendication 10, comprenant une résine de base de polyacétal et un polymère coeur-enveloppe ayant en tant que coeur un polymère caoutchouteux et en tant qu'enveloppe un copolymère vinylique vitreux ayant au moins un groupe polaire oxygéné, cette résine et ce polymère coeur-enveloppe ayant été mélangés à l'état fondu pour former une composition de résine de polyacétal moulable à faible brillant de surface.
- 10 12. Composition selon la revendication 10 ou 11, dans laquelle la résine de base est un homopolymère ou copolymère de polyacétal.
- 15 13. Article moulé en résine de polyacétal à faible brillant de surface, qui comprend une composition de résine de polyacétal telle que revendiquée dans l'une quelconque des revendications 10 à 12.

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